# V.A.7 Component Benchmarking Subtask Reported: USFCC Durability Protocol Development and Technical-Assisted Industrial and University Partners

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Project Start Date: October 2003 Project
End Date: Project continuation and direction determined annually by DOE

## Objectives

- Assist technically, as directed by DOE, fuel cell component and system developers.
- Test materials and components.
- Validate and compare single-cell test protocols (Japan Automotive Research Institute [JARI], European Union [EU], Korea, China).
- Provide support to the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE Freedom Cooperative Automotive Research (FreedomCAR) Fuel Cell Technology Team.
- Review, comment, and refine durability protocols as necessary.
- Validate technical findings as directed by DOE.

## Technical Barriers

This project can be directed to address any of technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, however in Fiscal Year 2008 it addressed:

(A) Durability
(B) Cost
(C) Performance
(G) Start-up and Shut-down Time and Energy/Transient Operation
(D) Water Transport within the Stack

## Technical Targets

In this particular task, any of the technical targets in Tables 3.4.2 – 3.4.14 may be addressed at any given time, depending upon the sub-topic in which developers are addressing. In FY 2008, it principally addressed:

- Durability with cycling: 5,000 hours
- Cost: $30/kW$_e$
- MEA - Electrode Performance: 1,000 mW/cm$^2$
- Cold start-up time (30 s to 50% rated power from -20°C, and 5 s from 20°C)
- Start-up and shut-down energy (5 MJ from -20°C, 1 MJ from 20°C)
- Unassisted start from low temperature (-40°C)

## Approach

- Provide specialized testing and characterization for funded DOE project developers on an as-directed basis.
- Provide testing of materials and participation in the further development and validation of a single-cell test protocols with the U.S. Fuel Cell Council (USFCC).
- Participation and technical assistance to the USCAR/FreedomCAR Fuel Cell Technology Team.
- Supply technical expertise to the Fuel Cell Tech Team as questions arise, focused on single-cell testing to support the development of targets and test protocols.
- Participation in working groups (such as Round-Robin Testing).
- Validate technical findings as directed by DOE.
- Validate and compare single-cell test protocols (JARI, EU, Korea, China).
- Review, comment, and refine durability protocols as necessary.

## Accomplishments

- Collaborated with more than 30 industrial, university, or laboratory partners.
- Provided test insight and/or results to several DOE-funded project investigators.
- Participated in the review and development of USFCC durability protocols.
- Participated in USFCC Accelerated Stress Testing (AST) Protocol Development Round Robin.
- Prepared and tested three 50 $cm^2$ fuel cells using LANL's MEA fabrication to compare JARI, EU and USFCC/LANL test protocols.
- Held multiple LANL Hands-On Fuel Cell Training Classes at no cost to interested parties.

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## Introduction

Our technically-assisted efforts over the past fiscal year included a variety of collaborators from the fuel cell community, including newly awarded DOE solicitation winners. They include affiliates from other government laboratories, universities, and industry. We have consistently reached out to the fuel cell community by offering training and workshops, honoring invited presentations, and visiting and hosting (potential) collaborators. Although a large portion of this effort goes unpublished, for proprietary reasons, there has been a significant thrust in developing and testing protocols. These protocols, single-cell and durability, are geared to standardize fuel cell testing to ensure reproducible results and to help address failure mechanisms, respectively. We have established an international testing rapport in yet another effort, where 'in-house' membrane electrode assemblies (MEAs) were prepared and tested using multiple protocols from the international collaborators.

## Results Highlights

Following are non-proprietary highlights of the technical assistance task for FY 2008.

### Round Robin Verification Development and Testing of JARI, EU, and USFCC/LANL Test Protocols

In 2007, several new DOE projects on impurity studies began. In an effort to effectively gauge the different test sites participating in these studies, LANL led a DOE round robin test. A test cell was initiated at LANL and passed along to different test sites for repeat tests. The cell would then be returned to LANL for final testing. The findings from this study eventually led to the test sites calibrating and/or refining their testing equipment. A 50 $cm^2$ fuel cell containing 0.2 mg Pt/$cm^2$ on each electrode, produced at LANL, was assembled and qualified according to the USFCC single cell test protocol [1]. Each test site generated multiple voltage-current (VI) curves according to the accompanying procedures. Figures 1 and 2 highlight these results. In Figure 1, the cell was operated at 80°C with 25 psig (at sea-level) backpressure and fully humidified hydrogen and air gases. The results from Figure 2 reflect testing at 60°C, ambient (at sea-level) backpressure, and 100% relative humidity (RH). In each case, the hydrogen and air utilizations were 80% and 50%, respectively. The University of Connecticut (UConn) and Clemson data overlap. While these results show good agreement, in earlier attempts (results not shown) problems developed in the test article. At one

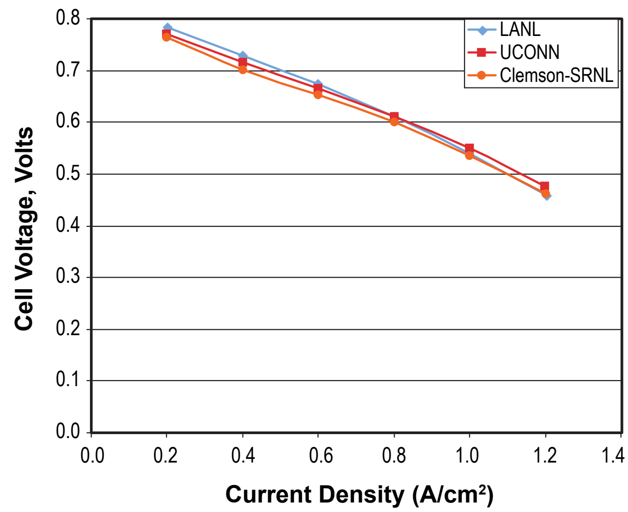


**FIGURE 1.** Comparison of VI Curves Generated at 80°C, 25 psig and 100% RH between LANL, UConn, and Clemson

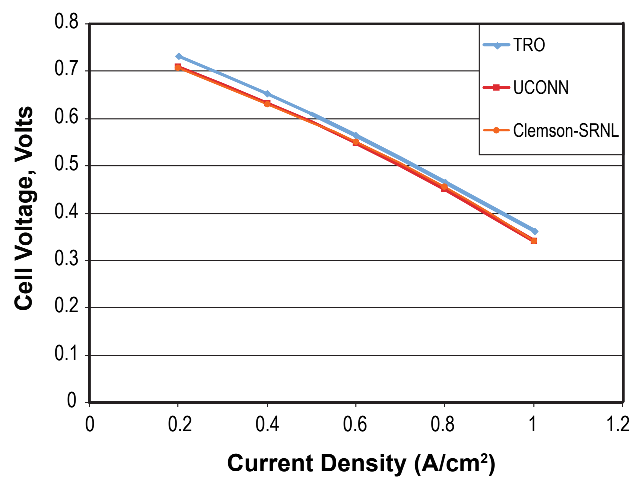


**FIGURE 2.** Comparison of VI Curves Generated at 60°C, 0 psig and 100% RH between LANL, UConn, and Clemson

of the test sites, a pinhole developed in the fuel cell. This was due to an out-of-range mass flow controller (MFC). The pinhole was verified using a leak test that was documented and shared with the test sites. The test site began using multiple MFCs, thus correcting the problem. At a different site, the results were considerably misaligned, approximately 100 mV at each current. After recalibrating their test stand, they retested and the results are included. The slight differences will be further investigated, but are assumed to be due to differences in humidification schemes, gas purity, and/or fluctuations in MFCs.

Besides the USFCC/LANL protocol, there are several international test protocols that exist for single-cell testing. To assure that differences in data produced are not due to the different break-in procedures, the JARI, EU and USFCC/LANL test procedures were compared. These tests are being conducted in parallel with the other protocol developers. Three identical 50 $cm^2$ fuel cells are to be tested following each protocol. In our hands, the findings show disagreement in the mass transport region. Subsequent tests are being conducted to evaluate the differences, although similar findings were presented at a non-public forum by another international test site.

## Performance and Durability Operating at Sub-Freezing Temperatures

Fuel cells in automotive applications will have to survive freeze-thaw cycles, and be able to start from freezing conditions. Thus, polymer electrolyte membrane (PEM) fuel cell operation with sub-freezing conditions is becoming an active area of research. DOE has stated targets for freeze survivability, start-up time and start-up energy from -20°C and 25°C. In support of a project funded specifically to develop fuel cell stacks to meet the DOE start-up targets, supporting measurements have been made to help define membrane conductivity at low (sub-freezing) temperatures. Figure 3 shows membrane conductivity as a function of temperature during cooling starting from an initial membrane hydration of 25% RH at 70°C. The data are plotted as membrane conductivity in SK (conductivity*temperature with units of Siemens*Kelvin). The bottom x-axis is 1/T ($K^{-1}$) with the top axis shown in °C (not linear). This measurement shows significant hysteresis in the membrane conductivity between cooling and heating. Also, note that as the cell was sitting at -40°C (for several hours), the membrane actually hydrated at the low temperatures, as evidenced by the increasing conductivity.

In comparison, Figure 4 shows membrane conductivity for a membrane starting with an initial hydration of 50% RH and 100% RH. At 100% RH and 70°C, the membrane is fully hydrated, and no hysteresis in conductivity is observed for the cooling/heating cycles. At 50% RH, the membrane water content is lower, and thus the conductivity is lower, however at cold temperature, the membrane hydrates probably because the RH at low temperatures is much higher (on a percentage basis).

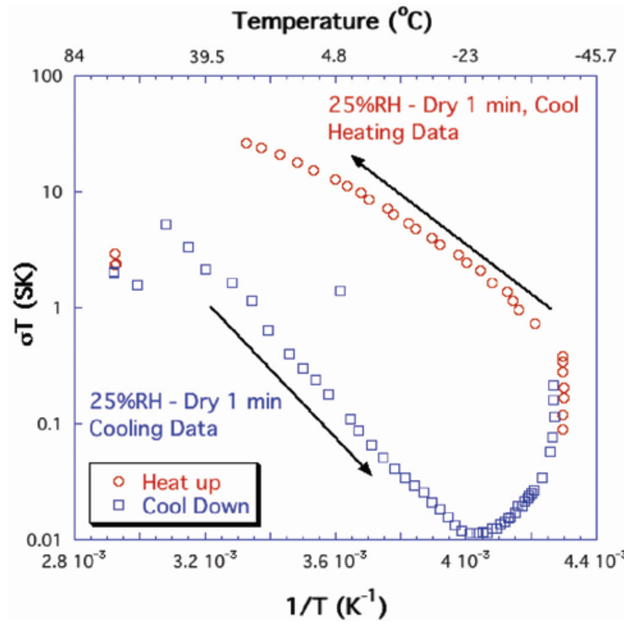


**FIGURE 3.** Membrane Conductivity Measurements during Cooling to -40°C and Subsequent Heating (Materials supplied by Nuvera Fuel Cells. Initial MEA condition of 25% RH.)

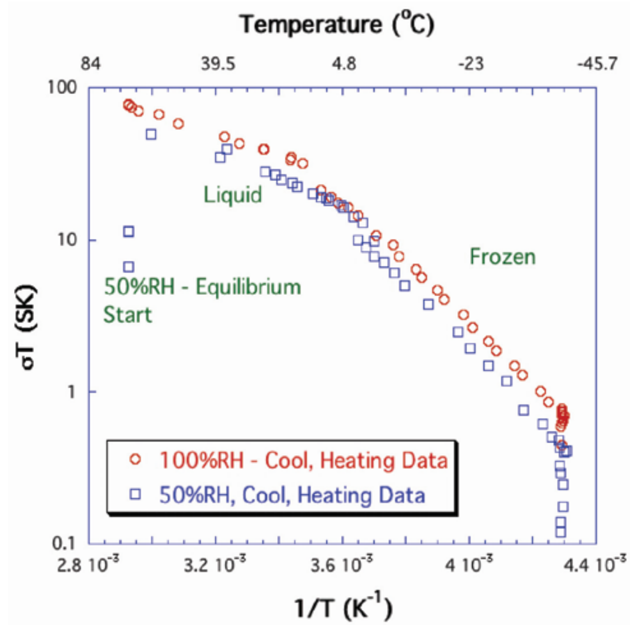


**FIGURE 4.** Membrane Conductivity Measurements during Cooling to -40°C and Subsequent Heating (Materials supplied by Nuvera Fuel Cells. Initial MEA condition of 50% RH.)

## Water Profiles by Neutron Imaging

High resolution neutron radiography images of water profiles in operating fuel cells were obtained using standard MEA materials (such as Nafion® 212) and specialized materials provided by industrial collaborators (including W.L. Gore and 3M), and a laboratory research material (block polysulfone ether polymers [BPSH] hydrocarbon membrane). These measurements were taken using newly developed hardware from LANL.

Figure 5 shows the relative water content in a cross-section profile of the materials to compare the in situ water content of the various materials under close to identical operating conditions. Note that the membrane/catalyst layer is only about 5 pixels wide for the N212 MEA, and less for thinner MEAs. The measured water content in the Nafion® material is lower than expected by equilibrium measurement of Nafion® water uptake [2]. Also, the water content in the Gore Primea MEA, and 3M NSTF should be similar, as the actual membrane material is essentially identical. This discrepancy may be due to the neutron detector spread function. While the absolute water content for these thin structures needs better quantification, the relative amounts of water in the MEA structure provides information to developers to help develop better methods for water management within their MEA structures and for specific materials, such as hydrocarbon membranes.

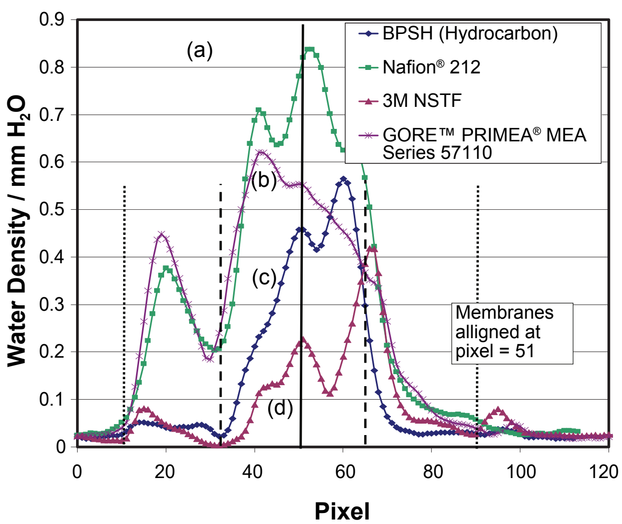


**FIGURE 5.** Water Profiles Measured by Neutron Imaging (Comparison of water content in different MEA/membrane materials: (a) Nafion® 212, (b) Gore Primea® MEA, (c) BPSH, (d) 3M NSTF. Cell temperature of 80°C.)

## Future Work

Continue to technically assist fuel cell component and system developers, as directed by DOE, to meet 2010 and 2015 technical targets.

## FY 2008 Publications/Presentations

1. Rockward, T., FCTES$^{QA}$ Update Meeting, Jan. 23, 2008. Golden, CO.
2. Borup, R., '3M Cell Neutron Radiography,' Presentation to 3M, Feb 12, 2008, Detroit, MI.
3. Borup, R., 'Water Transport Exploratory Studies,' Presentation to W.L. Gore, June 17, 2008, Newark, Delaware.
4. Mukundan, R., 'Sub-Freezing Effects on Fuel Cell performance and Durability' Presentation to W.L. Gore, June 17, 2008, Newark, Delaware.

## References


1. www.usfcc.com
2. T.A. Zawodzinski, Jr., C.Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, and S. Gottesfeld, *Water Uptake by and Transport Through, Nafion® 117 Membranes, J. Electrochem. Soc.,* Vol. 140, No. 4, 1993.